

Charge-density wave, superconductivity and f -electron valence instability in EuBiS_2F

Hui-Fei Zhai,^{1,*} Zhang-Tu Tang,^{1,*} Hao Jiang,^{1,*} Kai Xu,¹ Ke Zhang,¹ Pan Zhang,¹
Jin-Ke Bao,¹ Yun-Lei Sun,¹ Wen-He Jiao,¹ I. Nowik,² I. Felner,² Yu-Ke Li,³ Xiao-Feng
Xu,³ Qian Tao,¹ Chun-Mu Feng,¹ Zhu-An Xu,^{1,4,5} and Guang-Han Cao^{1,4,5,†}

¹*Department of Physics, Zhejiang University, Hangzhou 310027, China*

²*Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel*

³*Department of Physics, Hangzhou Normal University, Hangzhou 310036, China*

⁴*State Key Lab of Silicon Materials, Zhejiang University, Hangzhou 310027, China*

⁵*Center for Correlated Matter, Zhejiang University, Hangzhou 310027, China*

Superconductivity (SC) and charge-density wave (CDW) are two contrasting yet relevant collective electronic states which have received sustained interest for decades. Here we report that, in a layered europium bismuth sulfofluoride, EuBiS_2F , a CDW-like transition occurs at 280 K, below which SC emerges at 0.3 K, without any extrinsic doping. The Eu ions were found to exhibit an anomalously temperature-independent mixed valence of about +2.2, associated with the formation of CDW. The mixed valence of Eu gives rise to self electron doping into the conduction bands mainly consisting of the in-plane Bi-6*p* states, which in turn brings about the CDW and SC. In particular, the electronic specific-heat coefficient is enhanced by ~ 50 times, owing to the significant hybridizations between Eu-4*f* and Bi-6*p* electrons, as verified by band-structure calculations. Thus, EuBiS_2F manifests itself as an unprecedented material that simultaneously accommodates SC, CDW and f -electron valence instability.

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I. INTRODUCTION

Charge-density wave (CDW) and superconductivity (SC) are different collective electronic orders, although both are associated with Fermi surface instabilities owing dynamically to electron-phonon interactions (for conventional BCS superconductors). CDW, usually occurring in low-dimensional materials, generally shows periodic modulations of conduction electron density and crystalline lattice in real space. In contrast, SC, appearing in materials not limiting to low dimensionality, exhibits an intriguing electronic ordering in momentum space due to condensation of Cooper pairs, without any static lattice deformation. Basically they are competing orders, nevertheless, coexistence of SC and CDW is frequently observed in low-dimensional systems by various experiments[1–3]. In recent years, the relationship between CDW and SC has become a hot topic in cuprate high-temperature superconductors[1, 4–7] as well as ‘conventional’ superconductors that bear CDW instability[1, 2, 8]. Currently, CDW is also considered as an intertwined electronic orders, not simply competing with SC[9].

Recently, SC was discovered in a quasi-two-dimensional (Q2D) bismuth chalcogenide, $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$ [10] (The chemical formulae is preferably written as $\text{LaBiS}_2\text{O}_{1-x}\text{F}_x$ according to standard nomenclature[11]). This new class of materials consists of BiS_2 bilayers that are believed to be responsible for

SC. Band structure calculations[12–15] reveal that the undoped parent compound LaBiS_2O belongs to a band insulator with an energy gap of ~ 0.8 eV[13–15]. The conduction bands near Fermi level consist mainly of in-plane Bi-6*p* orbitals. Upon electron doping, these conduction bands are partially filled, which leads to Q2D Fermi surface (FS) sheets. A minimal electronic model including Bi- 6*p_x* and 6*p_y* orbitals was thus constructed[12]. Interestingly, the resultant two bands have a Q1D character with a double minimum dispersion, making FS nesting possible. Possible CDW phases due to Q1D distortions of the Bi and/or S atoms were proposed for $x \sim 0.5$ [13, 15]. Nevertheless, except for an inflection point in the temperature dependence of resistivity in $\text{La}_{0.9}\text{M}_{0.1}\text{BiS}_2\text{O}$ ($M=\text{Th, Ti, Zr and Hf}$), which was speculated to be related to a CDW effect[16], no more signatures in physical properties for a CDW transition have been observed so far.

Here we report a series of evidences for a CDW transition at $T_{\text{CDW}} \sim 280$ K in an isostructural compound, EuBiS_2F , synthesized for the first time. Unlike other parent compounds such as LaBiS_2O [17] and SrBiS_2F [18] that are undoped insulators, surprisingly, EuBiS_2F itself is metallic, and moreover it exhibits SC below 0.3 K. By various experimental approaches, we demonstrate that EuBiS_2F is actually self doped due to partial electron transfer from the Eu ions to the BiS_2 bilayers. The Eu ions exhibit an anomalously temperature-independent mixed valence of about +2.2. The electronic specific-heat coefficient extracted from the experimental data is as large as $73 \text{ mJ K}^{-2} \text{ mol}^{-1}$, ~ 50 times larger than those of its analogues, suggesting significant hybridizations between Eu-4*f* and Bi-6*p* electrons. Therefore,

* These authors contribute equally to this work.

† Correspondence should be sent to: ghcao@zju.edu.cn

to our knowledge, EuBiS_2F represents the first material that simultaneously bears SC, CDW and f -electron valence instability.

II. EXPERIMENTAL METHODS

a. Sample's synthesis The EuBiS_2F polycrystalline sample was synthesized by a solid-state reaction in sealed evacuated quartz tubes. All the starting materials were bought from Alfa Aesar. The stoichiometric mixtures of EuS [presynthesized by reacting Eu (99.9%) and S (99.9995%) pieces in sealed evacuated quartz tubes at 1073 K for 20 h], EuF_2 (99.9%) and Bi_2S_3 (99.995%) powders, loaded in an evacuated quartz ampule, were heated in a muffle furnace to 1053 K for 20 h. The reacted mixtures were ground for homogenization in an agate mortar, pressed into pellets, and sintered at 1053 K for another 20 h. This process was repeated until nearly single-phase sample was obtained. An argon-filled glove box was employed for the operations above to avoid the contamination of water and oxygen as far as possible.

b. X-ray diffractions and crystal structure Powder x-ray diffraction (XRD) was carried out at room temperature and at low temperatures down to 13 K on a PANalytical x-ray diffractometer (Model EMPYREAN) with a monochromatic $\text{CuK}\alpha_1$ radiation. The lattice parameters were precisely determined using Si powders as the internal standard reference material. The crystal structure was refined based on the CeBiS_2O -type structure model[19] by a Rietveld analysis using the code Rietan-2000[20]. With the exact lattice parameters, all the structural refinements were easily convergent. The resultant weighted reliable factor R_{wp} is 7.1–9.0%, and the 'goodness of fit' parameter S is 1.1–1.5, indicating good reliability for the refined crystal structure.

c. Physical property measurements The electrical resistivity was measured with a standard four-electrode method on a Quantum Design PPMS-9. The as-prepared EuBiS_2F pellet was cut into a thin bar with a dimension of $2.0 \times 1.6 \times 0.6 \text{ mm}^3$, and gold wires ($\phi = 30 \text{ }\mu\text{m}$) were attached onto the sample's surface with silver paint. The size of the contact pads produces a total uncertainty in the absolute values of resistivity of 15%. A dilution refrigerator was employed for measuring the resistivity at ultra low temperatures down to 20 mK with an electric current of 20 μA . Hall coefficient was measured by permutating the voltage and current electrodes[21] under a magnetic field of 60 kOe, and the results were checked by a standard field-sweep measurement. The heat capacity was measured using a relaxation method on a PPMS-9. The dc magnetization was measured on a Quantum Design MPMS-5 equipment. Signals from the sample holder were carefully removed.

d. Mössbauer spectroscopy Mössbauer studies on ^{151}Eu at various temperature (up to 388 K), were performed by using a conventional constant acceleration drive and $\sim 50 \text{ mCi } ^{151}\text{Sm}_2\text{O}_3$ source. All spectra ob-

tained were analyzed in terms of least square fit procedures to theoretical expected spectra. The experimental spectra were analyzed by two Lorentzian lines from which values for the isomer shift (S) and the spectral area of the resonance absorption lines were derived. The analysis considered also the exact shape of the source emission line[22]. The velocity calibration was performed with an α -iron foil at room temperature and the reported S values are relative to Eu_2O_3 at room temperature.

e. Electronic structure calculations We carried out electronic structure calculations using the Vienna Ab-initio Simulation Package (VASP)[23]. The experimental crystal structure parameters at 15 K were employed for the calculations. The strong Coulomb repulsion of the $\text{Eu-4}f$ electrons was included using local spin density approximation plus a U parameter (LSDA+ U). The plane-wave basis energy cutoff was set at 540 eV.

III. RESULTS AND DISCUSSIONS

A. Crystal structure and bond valence sum of Eu

EuBiS_2F crystallizes in the tetragonal CeBiS_2O -type structure[19] with space group $P4/nmm$ (No. 129). The crystal structure, as depicted in the top inset of Fig. 1(a), can be viewed as an intergrowth of fluorite-like Eu_2F_2 block layers and NaCl -like BiS_2 bilayers along the crystallographic c axis. The XRD patterns for the EuBiS_2F sample were well reproduced using the crystal structure model by Rietveld refinement[20]. No obvious extra reflections appear, indicating monophasic EuBiS_2F within the XRD detecting limit ($\sim 2 \text{ wt.}\%$ in normal conditions).

The refined structural data were tabulated in Table S1 of the Supplemental Material (SM)[24]. The room-temperature lattice parameters a [$=4.0508(1) \text{ }\text{\AA}$] and c [$=13.5338(3) \text{ }\text{\AA}$] are 0.7% and 2.1% smaller, respectively, than the counterparts of SrBiS_2F [$a=4.079(2) \text{ }\text{\AA}$ and $c=13.814(5) \text{ }\text{\AA}$][18]]. As a consequence, the c/a ratio of EuBiS_2F [3.341(1)] is remarkably reduced, compared with those (~ 3.39) of other CeBiS_2O -type parent compounds. Since the c/a value decreases upon electron doping for the CeBiS_2O -related systems[10, 25–29], one may speculate that EuBiS_2F could be self electron doped (see previous examples of self doping in Refs. [30, 31]) owing to possible mixed valence of Eu. An alternative approach to verify this speculation is to calculate the bond valence sum[32] of Eu (Eu-BVS) by the formulae $\sum \exp(\frac{R_0 - d_{ij}}{0.37})$, where R_0 is empirical parameters (2.04 \AA and 2.53 \AA for Eu-F and Eu-S bonds, respectively[32]) and d_{ij} denotes the measured bond distances between Eu and the *nine* coordinating anions. The resultant Eu-BVS values are 2.14(2) – 2.18(2), weakly depending on temperature (in comparison, the Sr-BVS value in SrBiS_2F is calculated to be 2.05(4) at based on the crystallographic data in Ref. [18]). This means that the BiS_2 bilayers are indeed self doped, accounting in turn for the anomalously small c/a ratio in EuBiS_2F .

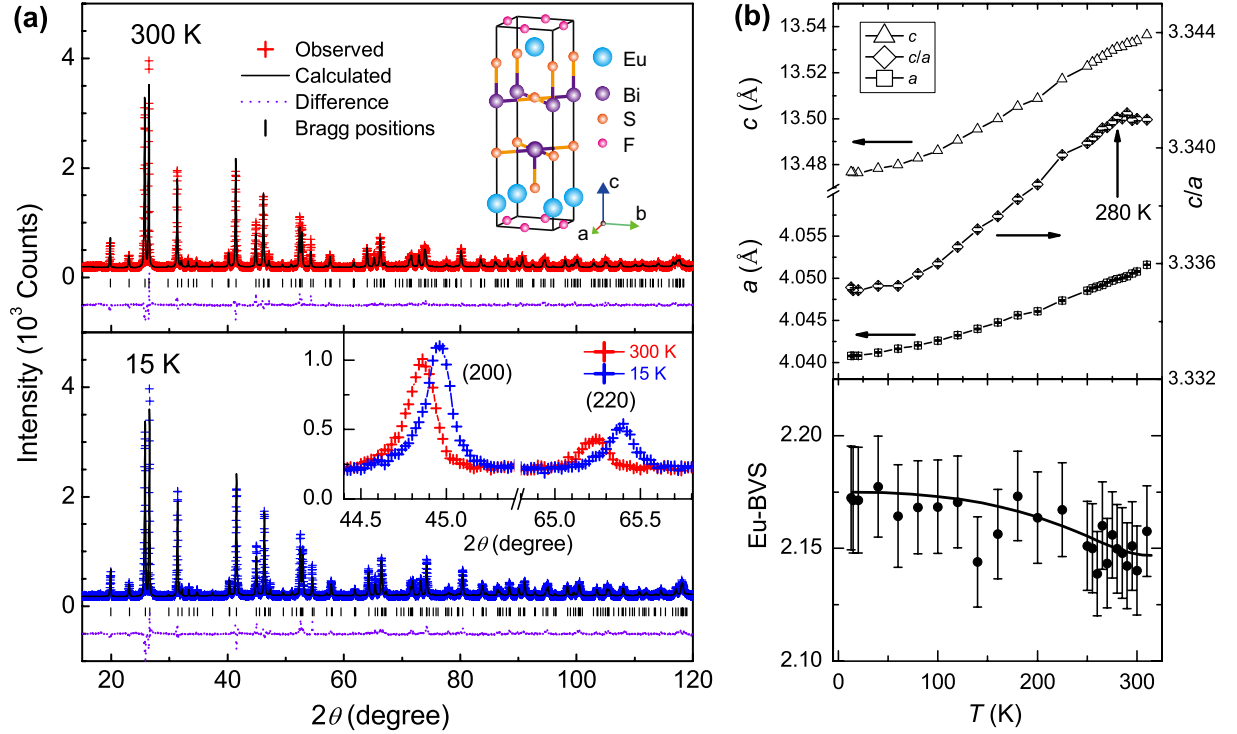


FIG. 1. Crystal structure and its temperature dependence for EuBiS₂F. (a) Powder x-ray diffractions and their Rietveld refinement profiles at 300 K (top) and 15 K (bottom). Top inset: the crystal structure of EuBiS₂F. Bottom inset: an enlarged plot showing the (200) and (220) reflections. (b) Temperature dependence of lattice parameters a , c , c/a , and the bond valence sum of Eu (Eu-BVS). The solid line is a guide to the eye.

In order to detect the possible superstructured CDW phase predicted[13, 15], we performed low-temperature XRD measurements down to 13 K. No splitting for the (200) or (220) peak was detectable, as seen in the bottom inset of Fig. 1(a). Also, the structural fittings using the superstructures of $\sqrt{2} \times \sqrt{2} \times 1$ [13] (with space group $Cmma$) or $\sqrt{2} \times 2\sqrt{2} \times 1$ [15] (with space group $P2_12_12$) could not give a better refinement. Although static long-range CDW order cannot be detected by the conventional XRD technique, considering the strong evidences for a CDW transition at 280 K (see the following sections), we suppose that a dynamic and/or short-range CDW ordering is still likely. Indeed, theoretical calculations[13] indicate shallowness of the double-well potential with respect to the in-plane S(1) displacement, which leads to absence of static CDW order. Further experimental investigations with other techniques such as synchrotron XRD and electron diffractions at low temperatures are expected to be helpful to clarify this issue.

Figure 1(b) show temperature dependence of the crystal structural parameters and the Eu-BVS. The lattice parameters a and c decrease monotonically with decreasing temperature. A subtle anomaly around 280 K can be detected, and it is more evident in c/a ratio. As stated above, the decrease in c/a means more electron doping on the BiS₂ bilayers. Thus, the small decrease in c/a below 280 K suggests further electron transfer from the

Eu atoms to the BiS₂ bilayers with decreasing temperature. Indeed, the Eu-BVS value exhibits a detectable variations. At lower temperatures, both c/a and Eu-BVS saturate, indicating a stable mixed-valence state for Eu.

B. Electrical transport properties

Figure 2 shows the temperature dependence of resistivity, $\rho(T)$, for the EuBiS₂F polycrystalline sample. Unlike the parent compound SrBiS₂F that shows semiconducting behaviour[18, 29], EuBiS₂F is virtually metallic, due to the self doping effect. More surprisingly, the $\rho(T)$ curve exhibits a broad hump below ~ 280 K, resembling the CDW transitions in Q2D systems like Cu_xTiSe₂[8]. The resistivity anomaly cannot be ascribed to the increase of the Eu valence, because the latter would generate more electron carriers in the conducting BiS₂ bilayers, which would lower (rather than raise) the resistivity. Moreover, the hump is not even related to the Eu-4*f* electrons, because we observed a similar hump, due to the CDW instability, in an Eu-free sample (Sr_{0.7}Ca_{0.3})_{0.75}La_{0.25}BiS₂F (see Fig. S1 in the SM[24]). Therefore, this $\rho(T)$ hump is interpreted by a gap (probably a pseudogap) opening at Fermi level (E_F) because of the formation of dynamic/short-range CDW below 280 K. Here we note that no obvious nonlinear $I-V$ relations

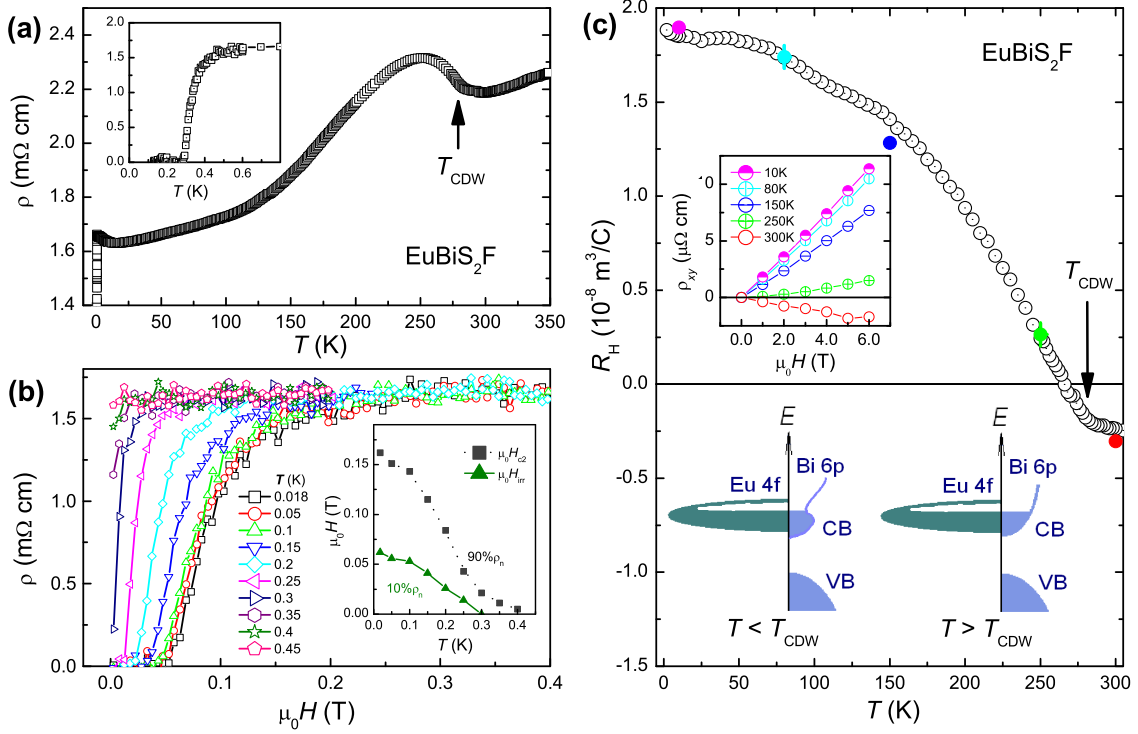


FIG. 2. Electrical transport properties and superconductivity in EuBiS_2F . (a) Temperature dependence of resistivity showing a CDW-like anomaly at 280 K and superconductivity at 0.3 K (inset). (b) The magnetoresistivity as a function of magnetic field at low temperatures. The inset plots the upper critical field, H_{c2} , by the criteria of $90\%\rho_n$, where ρ_n stands for the normal-state resistivity. (c) Temperature dependence of Hall coefficient in which a turning point at 280 K is seen. Upper inset: field dependence of Hall resistivity at some fixed temperatures. Bottom inset: schematic energy-band diagrams for $T < T_{\text{CDW}}$ (left) and $T > T_{\text{CDW}}$ (right), respectively. CB (VB) denotes the conduction band (valence band) in the BiS_2 bilayers.

associated with the sliding of CDW was observed down to 2 K.

At lower temperatures, a superconducting transition takes place with a zero-resistance temperature of 0.3 K at zero field [see the inset of Fig. 2(a)]. The superconducting transition temperature T_c is reduced by a factor of 10, compared with the BiS_2 -based superconductors synthesized under ambient pressure [25–29]. This could be due to the formation of CDW which loses partial FSs, relatively low electron doping, and pair breaking by the Eu magnetic moment. The superconducting transition was also demonstrated by the magnetoresistivity measurement at fixed temperatures, as shown in Fig. 2(b). The upper critical fields (H_{c2}) were determined using the criteria of $90\%\rho_n$, where ρ_n stands for the normal-state resistivity. The temperature dependence of H_{c2} shows positive curvature below T_c , possibly due to large anisotropy in H_{c2} [33] (note that the sample is polycrystals). The $\mu_0 H_{c2}$ value at 0.018 K is 0.16 T, which is obviously smaller than the Pauli limiting field, $\mu_0 H_P = 1.84 T_c \approx 0.4 T$.

To further understand the anomaly around 280 K in $\rho(T)$, we measured the temperature dependence of Hall coefficient (R_H). As shown in Fig. 2(c), at room temperature, R_H is negative, indicating dominant electron

transport. If assuming single band scenario, the carrier density is estimated to be $n = 1/e|R_H| = (2.1 \pm 0.3) \times 10^{27} \text{ m}^{-3}$, equivalent to a Hall number of $V_{\text{cell}}/(2e|R_H|) = 0.24 \pm 0.03$ electrons per formula unit (fu). This electron density corresponds to an Eu valence of $+2.24(3)$, if assuming that all the electron carriers in the conduction band (CB) come from the Eu-4f orbitals [see the schematic energy-band diagrams in Fig. 2(c)]. Below 280 K, R_H increases steeply, and then it changes the sign at lower temperatures. This peculiar $R_H(T)$ behaviour strongly suggests FS reconstructions owing to a CDW transition. In $\text{Sr}_{1-x}\text{La}_x\text{BiS}_2\text{F}$ system, as a comparison, the $R_H(T)$ is either positive (for $x \leq 0.45$) or negative (for $x \geq 0.5$) [29, 34, 35]. We speculate that a pseudogap opens below T_{CDW} , which could lower the E_F a little, as shown in the left diagram in Fig. 2(c). As a result, more transferred electrons are expected, accounting for the small increase of Eu valence below 280 K.

C. Magnetic properties

The magnetic properties Eu^{2+} and Eu^{3+} ions are very different because of different electron filling on the 4f orbitals ($4f^7$ and $4f^6$, respectively). The ground state

of the former is $^8S_{7/2}$ with an effective local-moment of $g\sqrt{S(S+1)}=7.94$ (μ_B). In contrast, the ground state of the latter is 7F_0 , which has zero magnetic moment. Nevertheless, the excited states 7F_J ($J=1, 2, \dots, 6$), due to the spin-orbit interaction $\lambda \mathbf{L} \cdot \mathbf{S}$, give rise to appreciable Van Vleck paramagnetic susceptibility (χ_{vv})[36]. Here the coupling constant λ also measures the energy of the first excited state. The λ value is 480 K for free Eu^{3+} ions[36], and it has a small change in solids, e.g., $\lambda=471$ K for EuBO_3 and $\lambda=490$ K for EuF_3 [37]. Consequently, the $\chi_{vv}(T)$ is featured by a temperature-independent plateau in the low-temperature regime (say, $T \leq 100$ K), and Curie-like paramagnetism with an effective magneton number of 3.4 per Eu^{3+} for high-temperature region ($T > 200$ K)[37]. In EuBiS_2F system, therefore, we can correctly analyze the temperature dependence of magnetic susceptibility, $\chi(T)$, with an extended Curie-Weiss law,

$$\chi = \chi_0 + C/(T + \theta_N). \quad (1)$$

In the low-temperature limit, the first term χ_0 includes χ_{vv} , in addition to Pauli paramagnetism (and Landau diamagnetism) of conduction electrons and Langevin diamagnetism from the core-shell electrons of all the constituent elements. At the high-temperature side, χ_{vv} is included to the second term, where C denotes Curie constant and θ_N is termed as paramagnetic Neel temperature. One may obtain the effective moment by the formulae $\mu_{\text{eff}} = \sqrt{3k_B C/N_A}$, where k_B and N_A denote Boltzmann and Avogadro constants, respectively.

Figure 3(a) shows the temperature dependence of magnetic susceptibility, $\chi(T)$, for the EuBiS_2F sample at $T \leq 100$ K. No magnetic transition is evident down to 2 K. The $\chi(T)$ data can be well fitted by Eq. (1), except for minor deviations below 10 K. The fitted effective paramagnetic moment is $7.2 \mu_B \text{ fu}^{-1}$, which means that the concentration of Eu^{2+} is 83% (hence the Eu valence is +2.17, fully consistent with the Eu-BVS value above). The Eu^{3+} ions (with a population of 17%) should give considerable contribution to χ_0 . Indeed, the fitted χ_0 value is as large as $0.0032(2) \text{ emu mol}^{-1}$. By referring to the Van Vleck susceptibility of EuF_3 ($\sim 0.006 \text{ emu mol}^{-1}$ below 100 K) in which the Eu valence is totally 3+[37], the χ_{vv} value of EuBiS_2F is then estimated to be $0.001 \text{ emu mol}^{-1}$ below 100 K. Since the Langevin diamagnetic susceptibility is negligibly small (about $-1.5 \times 10^{-4} \text{ emu mol}^{-1}$)[38] within the fitting errors, then, the Pauli susceptibility can be roughly estimated to be $\sim 0.002 \text{ emu mol}^{-1}$. This unusually large value of Pauli susceptibility suggests substantial hybridizations between Eu-4*f* and CB (see band structure calculations in Section III F).

Figure 3(b) shows the high-temperature range of $\chi(T)$, which was also fitted with Eq. (1). The fitting gives smaller χ_0 but larger C values, because χ_{vv} is now included in the second term of Eq. (1). By subtraction of the fitted curve from the experimental data, the residual susceptibility $\Delta\chi$ shows a hump-like anomaly where the magnetic susceptibility tends to drop [by $(5 \pm 2) \times 10^{-5}$

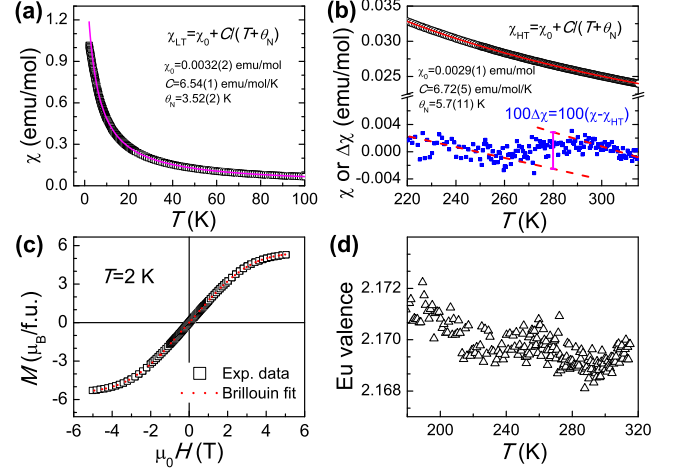


FIG. 3. Magnetic properties of EuBiS_2F . Temperature dependence of the dc magnetic susceptibility [(a): $T \leq 100$ K; (b): $T \geq 220$ K]. The solid lines are the fitted curves. The difference (multiplied by 100) between the experimental data and the fitted ones is shown in the lower part of (b). (c) Field dependence of magnetization at 2 K. The dotted line is a Brillouin fit. (d) The Eu valence estimated by the magnetic susceptibility. See details in the text.

emu mol^{-1}] at around 280 K. At first sight, it seems to be related to the change in Eu valence. However, similar hump in χ was also observed in an Eu-free analogous sample ($\text{Sr}_{0.7}\text{Ca}_{0.3}$) $_{0.75}\text{La}_{0.25}\text{BiS}_2\text{F}$ (see Fig. S2 in the SM[24]). Thus we speculate that the 'drop' of χ at 280 K is mainly resulted from the loss of Pauli paramagnetic susceptibility when a (pseudo)gap opens at the CDW transition. Here we note that the decrease of $N(E_F)$ in the CDW phase for $\text{LaBiS}_2\text{O}_{0.5}\text{F}_{0.5}$ calculated[15] is just equivalent to the loss of Pauli magnetic susceptibility.

The possible variation in Eu valence can be analyzed as follows. If P_{3+} denotes the concentration of Eu^{3+} [so that the fraction of Eu^{2+} is $(1 - P_{3+})$], one may calculate P_{3+} by the relation,

$$\chi = \chi_0 + P_{3+} \frac{C_{3+}}{T} + (1 - P_{3+}) \frac{C_{2+}}{T + \theta_N}. \quad (2)$$

With $C_{2+}=7.875 \text{ emu mol}^{-1} \text{ K}^{-1}$ and $C_{3+}=1.45 \text{ emu mol}^{-1} \text{ K}^{-1}$ [37], the Eu valence was obtained as plotted in Fig. 3(d). One sees that the Eu valence does not change so much around 280 K, but it tends to increase rapidly below 220 K, which is quantitatively consistent with the Eu-BVS values shown in Fig. 1(b).

One may also obtain the information of Eu valence from the field-dependent magnetization at 2 K [Fig. 3(c)] which shows a saturation at high magnetic fields. The saturation magnetization is significantly smaller than the expected value ($gJ=7.0 \mu_B \text{ fu}^{-1}$) for Eu^{2+} ions only. By fitting the $M(H)$ data using a Brillouin function with consideration of Weiss molecular field $B_{\text{mf}} = \xi M$, the saturation magnetization is determined to be $5.58 \mu_B \text{ fu}^{-1}$, corresponding to the Eu valence of +2.20, consistent with

the conclusion from the Curie-Weiss fitting above. The fitted parameter ξ is a negative value (-0.40), reflecting dominant antiferromagnetic interactions among the Eu localized moments, also agreeing with the positive value of θ_N in Eq. (1).

D. Mössbauer spectroscopy

Mössbauer spectroscopy (MS) is a powerful technique to study the Eu valence. The isomer shift S of the nuclei of Eu^{2+} and Eu^{3+} ions falls in two nonoverlapping ranges: $S_{2+} = -7.7 \sim -13.5 \text{ mm s}^{-1}$ and $S_{3+} = -0.01 \sim +2.6 \text{ mm s}^{-1}$ (relative to Eu_2O_3). Thus, MS easily identifies the valence state of Eu and, in the case of inhomogeneous mixed valence, the concentration of each Eu species can be determined by the relative absorption intensity. For the fast valence fluctuation (VF) scenario, the mean Eu valence can also be quantitatively evaluated by the change in S [39]. MS may also supply information on quadrupole and magnetic interactions.

Figure 4(a) shows the ^{151}Eu Mössbauer spectra at some typical temperatures of 90, 200, 297 and 388 K. At low temperatures (90 and 200 K), two absorption lines (or peaks) appear at -13.5 and -0.5 mm s^{-1} , which are obviously identified to the Mössbauer resonance absorptions of Eu^{2+} and Eu^{3+} nuclei, respectively. Since there is only one equivalent site in the crystal structure even at low temperatures, the two separate lines indicate slow Eu VFs (or even static charge ordering of Eu^{2+} and Eu^{3+}) with the time scale of $\tau_{\text{vf}} > 10^{-8} \text{ s}$ (note that the probing time of MS is about 10^{-9} s). The intensity of the minor line is about 1/3 of the major one, therefore, the mean Eu valence is $\sim +2.25$, basically consistent with the above conclusion drawn from the crystal structure and magnetic data. As the temperature is increased to 297 K, the intensity of the Eu^{3+} line decreases. Simultaneously, the two absorption lines get closer, and the line width is abnormally large (up to 5 mm s^{-1}). This fact suggests Eu VFs with the characteristic τ_{vf} close to 10^{-9} s , associated with the electron hopping between Eu^{2+} and Eu^{3+} . At 388 K, the Eu^{3+} line almost vanishes because the VFs are much faster. The isomer shift is then formulated by $S_{\text{vf}} = (1 - P_{3+})S_{2+} + P_{3+}S_{3+}$. With $S_{\text{vf}} = -11.6 \text{ mm s}^{-1}$, $S_{2+} = -13.5 \text{ mm s}^{-1}$ and $S_{3+} = 0 \text{ mm s}^{-1}$, the Eu valence at 388 K can be estimated to be $+2.14(2)$.

By the data fitting using the exact shape of the emission spectrum of $^{151}\text{Sm}_2\text{O}_3$ and considering quadrupole interactions, we were able to obtain the refined S , the full linewidth at half maximum (Γ) and the peak intensities (I), which are plotted respectively in Fig. 4(b). All these MS parameters point to a transition at 280 K. The most prominent feature is that the Γ value is peaked at 280 K. The sharp decrease in Γ below 280 K suggests that the Eu VFs slow down, probably in connection with the dynamic CDW. The isomer shifts and the relative intensity of the minor line respectively reflect fast VFs with $\tau_{\text{vf}} < 10^{-9} \text{ s}$ and slow VFs with $\tau_{\text{vf}} > 10^{-9} \text{ s}$. At 273 K,

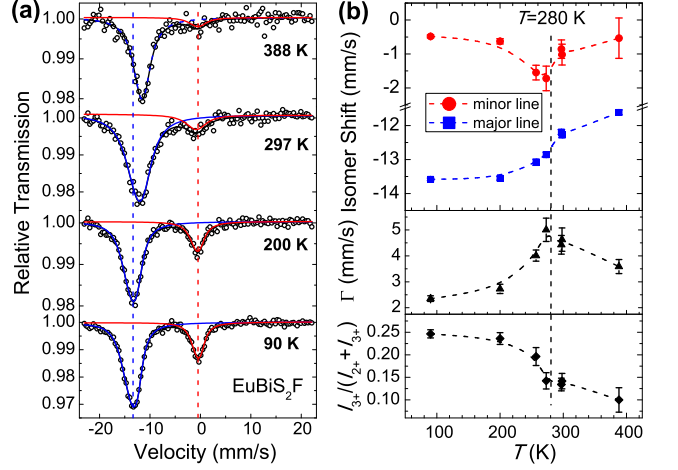


FIG. 4. Mössbauer result on EuBiS_2F . (a) ^{151}Eu Mössbauer spectra of EuBiS_2F at some typical temperatures. (b) Temperature dependence of the isomer shifts (top), absorption line width (middle), relative intensity of the minor line (bottom) from the data fitting of the ^{151}Eu Mössbauer spectra. The vertical dashed lines at -13.5 and -0.5 mm/s (a) and at 280 K (b) are guides to the eye.

for example, one may roughly estimated that 5(1)% of the Eu ions are in Eu^{3+} state with fast VFs, and 14(2)% of the Eu ions are in Eu^{3+} state with slow VFs. So, the overall Eu valence is $+2.19(3)$ at 273 K.

E. Specific heat

Heat capacity of a solid may supply important information not only for phase transition but also for electronic and magnetic states. Fig. 5(a) shows the temperature dependence of specific heat, $C(T)$, of EuBiS_2F . The $C(T)$ data tend to saturate to $120 \text{ J K}^{-1} \text{ mol}^{-1}$ at room temperature, consistent with the high- T limit for lattice specific heat (i.e., the Dulong-Petit value $3NR=15R=124.7 \text{ J K}^{-1} \text{ mol}^{-1}$, where N counts the number of elements per fu, R is the gas constant). One sees an anomaly around 280 K, a signal of second-order transition, further supporting a CDW-like transition.

In EuBiS_2F , the specific heat is contributed due to several different origins including crystalline lattice (C_{lat}), conduction electron (C_{el}) and Eu magnetism (C_{m}). One may correctly separate them out by considering different contribution weights in different temperature regions. Since no magnetic ordering takes place above 2 K, and the magnetic susceptibility well follows Curie-Weiss law above 10 K, C_{m} is then expected to be very small above 10 K at zero magnetic field. Therefore, we make use of a conventional approach, in which the low- T lattice contribution is taken as βT^3 , to extract C_{el} . The plot of C/T vs T^2 in the inset of Fig. 5(a) gives $\gamma=73.3 \text{ mJ K}^{-2} \text{ mol}^{-1}$ and $\beta=1.19 \text{ mJ K}^{-4} \text{ mol}^{-1}$. The resultant Debye temperature, $\theta_D = [(12/5)NR\pi^4/\beta]^{1/3}=201 \text{ K}$,

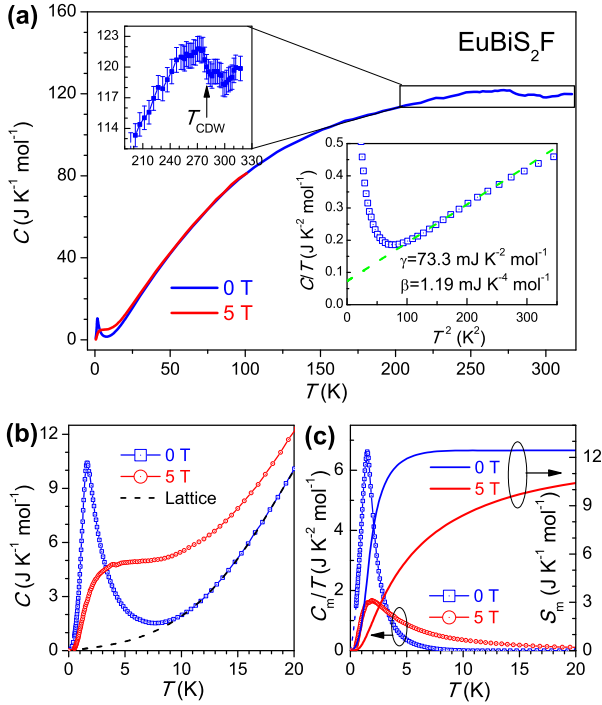


FIG. 5. Specific heat capacity for EuBiS_2F . (a) Temperature dependence of specific heat capacity, $C(T)$, from 0.5 to 320 K. Upper left inset: an enlarged plot of the $C(T)$ showing an anomaly at 280 K. Lower right inset: plot of C/T vs. T^2 at low-temperature region (the dashed line obeys $C/T = \gamma + \beta T^2$). (b) An enlarged plot of $C(T)$ from 0.5 to 20 K. The dashed line is a polynomial fit (see details in the text), representing the lattice contribution. (c) C_m/T (where C_m denotes magnetic contribution to the specific heat) and magnetic entropy S_m (left axis) as functions of temperature.

is reasonably in between with those of $\text{LaBiS}_2\text{O}_{0.5}\text{F}_{0.5}$ (221 K) and $\text{YbBiS}_2\text{O}_{0.5}\text{F}_{0.5}$ (186 K)[16], which vice versa guarantee the reliability of the Sommerfeld parameter. Notably, the fitted γ value is over 50 times of that of $\text{Sr}_{0.5}\text{La}_{0.5}\text{BiS}_2\text{F}$ ($1.42 \text{ mJ K}^{-2} \text{ mol}^{-1}$)[29]. Its corresponding $N(E_F) [= 3\gamma/(\pi k_B)^2]$ is as large as $30 \text{ eV}^{-1} \text{ fu}^{-1}$, which is about 25 times of the bare density of states of $\text{LaBiS}_2\text{O}_{0.5}\text{F}_{0.5}$ ($1.22 \text{ eV}^{-1} \text{ fu}^{-1}$)[14]. The greatly enhanced γ is related to the unusually large Pauli magnetic susceptibility above, mainly originating from the hybridization between conduction electrons and the Eu 4f electrons (see band structure calculations in Section III F).

Figure 5(b) zooms in the $C(T)$ data below 20 K. At zero magnetic field, a peak appears at 1.6 K with a high maximum up to $10.41 \text{ J K}^{-1} \text{ mol}^{-1}$. Under a magnetic field of 5 T, the peak is suppressed, forming a broad hump centered at about 3.5 K. Since the ground state of Eu^{2+} has zero orbital angular momentum, Schottky-like contribution is not expected. Hence the peak should be of magnetic origin. It is noted that, on the right side of the peak, there is no specific jump (or a divergence), as opposed to an ordinary long-range magnetic

ordering. This lets us consider that the specific anomaly comes from freezing of non-ordered Eu^{2+} spins, i.e., a spin glass transition. Similar observation was reported in $(\text{Eu},\text{Sr})\text{S}$ [40] and EuCu_2Si_2 [41]. To extract C_m below 10 K more accurately, the $C(T)$ data from 10 K to 20 K was fitted by a polynomial with odd-power terms, $C \approx C_{\text{el}} + C_{\text{lat}} = A_1T + A_3T^3 + A_5T^5 + A_7T^7$ (the resultant A_1 and A_3 agree well with the above γ and β values). Then the magnetic contribution C_m below 10 K was obtained by removing the contributions of C_{lat} and C_{el} . Consequently, the magnetic entropy can be calculated by $S_m = \int_0^T (C_m/T) dT$, as shown in Fig. 5(c), which is $12.4 \text{ J K}^{-1} \text{ mol}^{-1}$ at 20 K under zero field. Furthermore, nearly the same S_m value can be achieved under 5 T for integrating up to 60 K. The released magnetic entropy equals to 72% of $R \ln(2S+1)$ ($S=7/2$ for Eu^{2+}). Considered omission of magnetic entropy above 20 K, the resultant S_m value actually gives an upper limit of the Eu valence of +2.28 below 20 K.

F. Band structure calculations

To interpret above experimental results, we performed a first-principles calculation using local spin density approximation with consideration of on-site Coulomb interaction (LSDA+ U), particularly paying attention to the Eu-4f electronic states (the issue of CDW instability was well documented by Yildirim[15]). We first investigated the influence of the parameter U . Fig. 6(a) shows the variations of Eu-4f bands of EuBiS_2F with $U=0, 1, \dots, 6 \text{ eV}$. In all the cases, there is a large gap between occupied and unoccupied levels, as shown in the inset. Another prominent feature is that the highest occupied band (HOB) locates around E_F , regardless of the different U values. This fact suggests that the Eu-4f frontier occupied level in the HOB is pinned by the chemical potential of the conduction bands. The filled states in HOB actually represents Eu^{2+} , whilst the empty states in HOB, i.e., the 4f holes, correspond to Eu^{3+} .

Figure 6(b) shows the calculated band structure of EuBiS_2F with a realistic value of $U=3 \text{ eV}$. There are seven flat bands near E_F , all coming from the Eu-4f orbitals. The HOB crosses E_F , and hybridizes with the Bi-6p bands (see the zoom-in plot at the bottom). Furthermore, this HOB donates electrons to the Bi-6p bands, and leaves hole pockets around the \mathbf{M} point [see also the FS in Fig. 6(d)]. Consequently, although undoped, the CB of EuBiS_2F is filled with the transferred electrons. Due to the Q2D structure, cylindric-like FSs are presented [Fig. 6(d)]. Except for the 4f-hole pockets, two electron-type FS sheets appear around the \mathbf{X} point, similar to the case of $\text{LaBiS}_2\text{O}_{1-x}\text{F}_x$ with $x=0.25$ [12]. This 2D-like FS sheets have considerable nesting areas for developing CDW instability.

Figure 6(c) shows the calculated electronic DOS of EuBiS_2F . Obviously, the sharp peaks come from the Eu-4f orbitals. They are basically divided into two

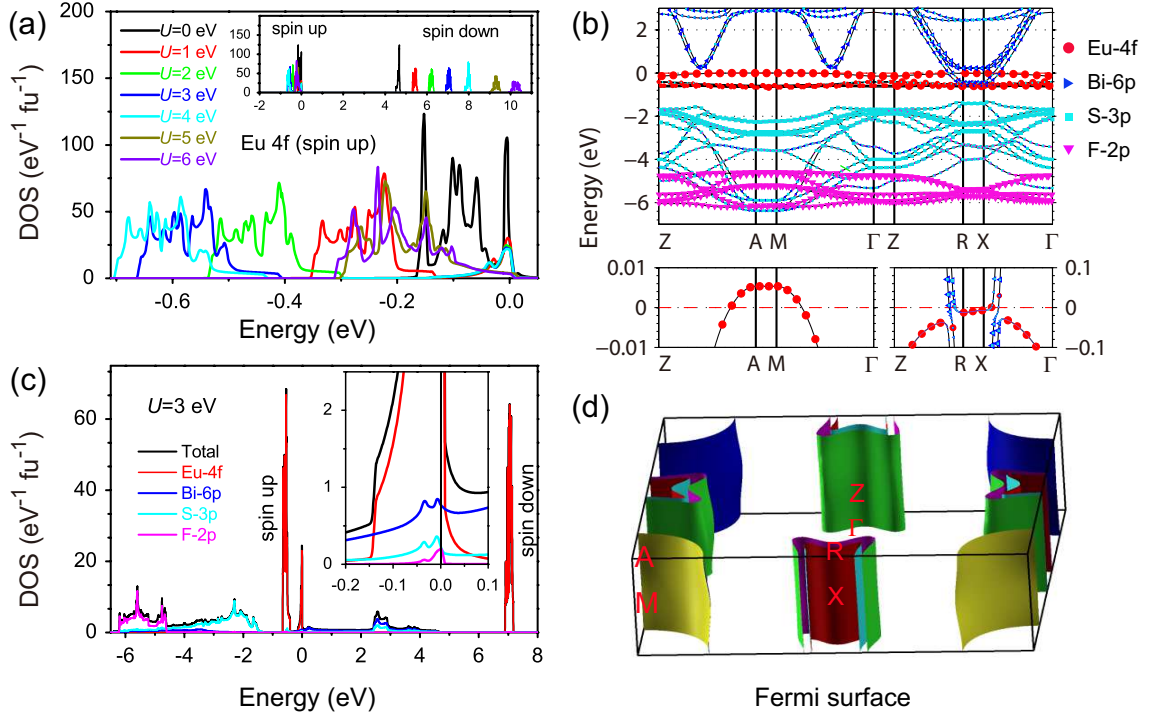


FIG. 6. Band calculations for EuBiS₂F using LSDA+ U method. (a) Variations of Eu-4 f bands with different U values. DOS denotes to density of states. (b) Calculated band structure of EuBiS₂F with $U=3$ eV. The contributions of the relevant orbital states are distinguished by different colors. The lower panels zoom in the band dispersions crossing the Fermi level ($E_F=0$). (c) Total and projected DOS with $U=3$ eV. Inset: an enlarged plot near E_F . (d) Fermi surfaces of EuBiS₂F derived from the band structure in (b).

groups, which are about 7 eV apart (corresponding to an effective Hubbard $U \sim 7$ eV). The frontier HOB nearby E_F is mainly contributed from the f_{xz^2} wave function. The DOS at E_F , $N(E_F)$, mainly comprises of Bi-6 p ($0.75 \times 2 \text{ eV}^{-1} \text{fu}^{-1}$) and Eu-4 f ($21.6 \text{ eV}^{-1} \text{fu}^{-1}$). The total $N(E_F)$ is about 20 times of that of LaBiS₂O_{0.5}F_{0.5}[14], well accounting for the enhancement of electronic specific-heat coefficient as well as Pauli susceptibility.

IV. CONCLUDING REMARKS

We have demonstrated a series of signatures for a CDW transition in EuBiS₂F, albeit no static long-range superlattice order was detected by XRD. They include a clear kink in the c/a ratio, a resistivity hump, a kink in Hall coefficient, a subtle magnetic susceptibility drop, and a specific-heat hump, all at $T_{\text{CDW}} \sim 280$ K. The slowing down of Eu VFs below T_{CDW} suggests a dynamic CDW ordering. Such a dynamic CDW is supported by the theoretical calculations which indicate dynamic in-plane displacements of S(1) owing to the shallowness of the double-well potential[13]. Very recently, 'checkerboard stripe' electronic state was observed on the cleaved surface of NdO_{0.7}F_{0.3}BiS₂ single crystals[42]. Although the nanoscale electronic inhomogeneity was considered to be

due to the atomic defects on the cleaved surface, it could be in some relations to the CDW instability.

As is known, CDW mostly originates from the FS nesting[1, 2]. Since the shape and the size of the FS sheets are predominantly decided by the electron filling in the CB of BiS₂-based materials[12], the electron doping level should be crucial for the occurrence of CDW. Our finding in EuBiS₂F implies that the CDW instability is optimized at around $x \sim 0.2$. To verify this point, we synthesized samples of (Sr,Ca)_{0.75}La_{0.25}BiS₂F, in which the electron doping was fixed to $x=0.25$. We indeed observed a similar CDW anomaly in this designed system (see Figs. S1 and S2 in SM[24]).

It is the mixed valence of Eu that considerable amount of electron carriers are transferred into the CB, which induces SC as well as CDW. Table I summarizes the Eu valence in EuBiS₂F determined via various methods at different temperature ranges. Basically, the Eu valence is about +2.2, nearly independent of temperature down to 2 K. This result is very unusual, since the Eu valence mostly increases remarkably with decreasing temperature, e.g., in the systems of EuM₂Si₂ ($M=\text{Cu}$ [39], Pd[43], Ir[44, 45]) and EuNi₂P₂[45, 46] where Eu VFs were present. As for the crystal structure of EuBiS₂F, there is only one crystallographic site for the Eu ions. Therefore, the mixed valence of Eu means existence of VFs. Indeed, according to the Mössbauer results above,

TABLE I. Summary of the Eu valence in EuBiS₂F determined via various methods in different temperature (T) ranges. Eu-BVS refers to bond valence sum[32] of the Eu ions. The number in parentheses represents the measurement uncertainty for the last digit.

Methods	Eu-BVS	Magnetization	Mössbauer	Heat capacity	Fermi surface
Eu valence	2.14(2)–2.18(2)	2.17(2)–2.20(1)	2.24(2); 2.19(3); 2.14(2)	< 2.28	2.25(5)
T (K)	310–13	300–2	≤ 200 ; 273; 388	0.5–20	N.A.

VFs are dominant above T_{CDW} . Around T_{CDW} , however, the VF frequency decreases rapidly. At temperature far below T_{CDW} , the VFs of Eu²⁺ and Eu³⁺ are slower than 10⁸ Hz. These observations suggest that Eu should have unequivalent Eu sites in short time scale, which could be realized in the proposed CDW phase with distortions of BiS layers[15]. Thus, the Eu valence is ‘pinned’ by the formation of CDW, resulting in the unique temperature-independent mixed-valence. In turn, the Eu VFs (no matter how slow they are) should be in favor of an unusual dynamic CDW state.

The emergence of SC under the CDW transition suggests that EuBiS₂F is also a CDW superconductor, like the well known NbSe₂[1–3]. The formation of CDW generally loses a portion of FSs, which leads to a decrease of T_c . In this sense, CDW competes with SC, as usual. However, an anharmonic model calculation[13] shows that the CDW instability is also essential for the SC, suggesting more profound relationship between SC and CDW.

Finally we would like to emphasize that the occurrence of SC at the (self) electron doping level corresponding to $x \sim 0.2$ is also surprising. Previous reports[34, 35] indicate that, in an analogous system of Sr_{1-x}La_xBiS₂F,

SC appears for $x > 0.3$, below which the samples show *insulating* behaviour, and the optimal doping is at $x \sim 0.5$. According to the band structure calculations[12–15], the FSs undergo a Lifshitz transition, characterized by a change in FS topology, with electron doping. The two doping levels, $x \sim 0.2$ and $x \sim 0.5$, have very different FS topologies. Therefore, the superconducting state in EuBiS₂F might be different from those of other BiS₂-based materials. It was predicted that[47], below the Lifshitz filling level (like the case of EuBiS₂F), the superconducting state is weak topological due to strong spin-orbit coupling. Further investigations are called for to verify this prediction.

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